Book Review

Reviews in Computational Chemistry, Volume 13. *Edited by Kenny B. Lipkowitz and Donald B. Boyd, Wiley–VCH, 1999, 426 pp. $139.00. ISBN 3-0-471-33135-X.*

Kenny Lipkowitz and Donald Boyd's highly successful series of *Reviews in Computational Chemistry* continues with its thirteenth volume. The first dozen contain reviews of topics that span the full range of computational chemistry, from relatively hard-core theoretical topics to those that are perhaps of more interest to computer scientists than chemists. This volume, despite its unlucky number, contains several excellent reviews that characteristically sample a wide range of topics. My knowledge of the subject material decreases approximately monotonically with chapter number in this volume. Accordingly, I learned the most from articles near the end and am perhaps most qualified to review those near the beginning. These comments should be considered in perusing my review.

Anyone who has ever done calculations on open-shell molecules has plenty of war stories to tell. Absurd vibrational frequencies, strange reaction energies, geometries that deviate from symmetries known from experiment to be maintained. What is truly remarkable is that most such results are presented in the literature with little qualification; those who do acknowledge the unphysical nature of the numbers generally rationalize it in overly simplistic and often technically incorrect ways. The review of Thomas Bally and Wes Borden should do much to educate computational chemists of the perils involved in the study of open-shell systems. The subjects of spin contamination, symmetry breaking, and second-order Jahn–Teller effects are hashed out in an appropriate level of detail and the strengths and weaknesses of various types of quantum chemical approaches (both *ab initio* and density functional methods) for these problems are analyzed. I find that the authors of this review share my opinions on a wide variety of topics. To name a few, they point out that restricted Hartree–Fock calculations are just as unreliable and perhaps more so than unrestricted treatments of radicals (albeit for different reasons); they seem to have an inherent distrust of second-order perturbation theory; and they make some important statements that are not often found in the literature (complete active space methods do not always remedy symmetry breaking problems; the stability of SCF solutions should be closely monitored). While all of the comments above refer to the the first part of the review, which deals exclusively with doublet radicals, a second part deals with the more difficult (in my opinion) problem of treating biradicals, where many methods that perform acceptably well for doublets are much less reliable. While I am more knowledgeable about the content of this review than the others that appear in this volume, I found very little to criticize. It would have been nice if the issues associated with orbital instabilities had been a bit more comprehensive, in particular the fact that near instabilities can be even more dangerous than highly unstable solutions; I thought that the authors are perhaps a bit too optimistic about the use of coupled-cluster methods for biradicals; and I would not have included QCISD in a discussion of configuration interaction methods. All in all, however, I have a highly favorable opinion of this review and feel that it should prove very useful to members of the community of computational chemists.

Neil Kestner and Jaime Combarize follow with a chapter on the well-known basis set superposition error (BSSE) problem in quantum chemistry. For the most part, this review covers the usual ground in describing how the BSSE affects calculated interaction potentials and how the counterpoise approach can be used to correct it. However, some newer ideas such as the use of localized orbital methods to reduce the BSSE and Mayer's chemical Hamiltonian approach are also introduced, discussed and critically evaluated. However, the question of whether one should use the full or virtual counterpoise procedure is left unresolved. The authors review some

Journal of Computational Chemistry, Vol. 21, No. 6, 505–507 (2000)

relevant literature on the subject including a study that concludes that the latter approach is best in correlated calculations, but then vehemently defend the alternative view (which they have previously favored in the literature) albeit in a way that leaves the question open. While there are a number of representative examples presented towards the end of the article, they are of the usual weakly-interacting system type. It might have been nice to see some other intriguing aspects of the BSSE problem such as the effect of intermolecular BSSE on vibrational potential functions (acetylene is a prominent example in which this seems to be important) and also perhaps the treatment of BSSE for charged species. At the same time, I cannot see how these additional topics could have been included in this review without it becoming unwieldy.

The following chapter presents a comprehensive review of quantum Monte Carlo methods (QMC) by James Anderson. While I was aware that a large number of distinctly different approaches fall under the umbrella of methods that use Monte Carlo techniques, this is the first time that I have found coherent descriptions of all approaches that I have seen in the literature. A particularly nice feature of this contribution is Anderson's use of the usual simple models of quantum mechanics—the particle in the box and the harmonic oscillator—to explain features of approaches that are designed to deal with the problems associated with nodes in QMC methods. After describing the methods, several applications are discussed. While most of these involve electronic structure calculations from systems ranging from the $H_2 + H$ transition state to transition states of cyclooctatetraene, two of them address the different problem of determining vibrational energy levels governed by a specific potential energy function. While some efforts are made to compare with other calculations in this chapter, attention seems to be entirely focused on "analytic variational methods" and density functional theory. However, the most accurate techniques used today are those based on coupled-cluster theory, and I would have enjoyed seeing some comparisons with these calculations. Notably absent from the discussion is the so-called R12-based CCSD(T) approach of Kutzelnigg and Klopper, which provides accuracy that is competitive with fixed-node QMC methods.

The review of Anders Wallqvist and Raymond Mountain taught me a lot about what goes into the development of model potentials used for treatments of liquid water in Monte Carlo and molecular dynamics simulations. They very carefully discuss the experimental measurement of properties that play a prominent role in the parametrization. This is followed by a fairly comprehensive discussion of the quantum mechanics of dispersion interactions (which incidentally are relevant to readers interested in the topic of BSSE that is reviewed earlier in the same volume). With this background in place, the authors introduce several models of water that illustrate their strengths, limitations and ranges of applicability. They do an admirable job of achieving their stated objective to "demystify the various potentials encountered in the literature and to help the reader make intelligent choices regarding simulations in which water is present." Given both the importance of liquid water, the vast amount of literature devoted to it, and the amount of information included in this review, the authors have done a good job in making things as concise as possible. While running 66 pages and including 261 references, two of the six reviews in the volume are longer.

James Briggs and Jan Antosiewicz follow with a chapter on the biologically important problem of ionization equilibria and how to best model the excruciatingly complex problems associated with pH-dependent phenomena in proteins and enzymes. The review discusses the usual finite-difference Poisson-Boltzmann equation approaches, and the combinatorial problem associated with the large number of possible ionization states of a given protein. The authors then go on to discuss several classes of issues and problems, such as the placement of hydrogen atoms in crystallographic protein structures, pH-dependent inhibitor binding, hydrogen exchange of amide groups, denaturation and dipole moments of proteins. Many of these concepts are illustrated by example calculations that appear towards the end of the chapter. The authors also mention a critique of the general methodology that is based on the assertion that it is inappropriate to assume that the dielectric constant is a constant within the protein. The authors devote about four pages to a balanced discussion of this critique and a defense of the assumption.

The final chapter deals with algorithms for the graphical representation of molecular structures, especially organic molecules. For structures that contain rings and especially for bicyclic and more complicated molecules, this is apparently a much more complex problem than I would have guessed. The issues involved in this field of "Structure diagram generation" are presented in detail by Harold Helson. While Helson provides the reader with a glossary of the surprisingly complicated lingo as-

sociated with this field, the text is still a relatively difficult read for outsiders. However, I'm sure it is extremely useful for those who work in this area. One feature of this review that I enjoyed is a discussion of the history of these approaches (it was interesting to see that some of the earliest programs were written in Fortran), along with some reproductions of figures that were made by programs a quarter-century ago. Finally, a survey of available software packages is presented in which Helson (an employee of CambridgeSoft, producer of the popular ChemDraw program) is admirably even-handed in describing both his own product and those of his competitors.

JOHN F. STANTON
Department of Chemistry
University of Texas
Austin, TX 78712